HOMO-LUMO, MEP, NBO, Vibrational and Thermodynamics Investigation on Phenylhydrazine using Quantum Computation and Molecular Spectroscopy Techniques

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ABSTRACT

The FT-Raman and FTIR spectra of Phenylhydrazine have been studied in the region 3500–50cm^{-1} and 4000–400 cm^{-1} respectively. The optimized geometry, vibrational frequency and corresponding intensity of Phenylhydrazine were achieved by the HF and DFT theory with 6-311G++ (d, p) basis set. In order to get correct vibrational frequency scale factor were used and compared with experimental FTIR and FT-Raman frequencies. The experimental spectra also match adequately with those of theoretically computed spectra. The electronic properties, like HOMO and LUMO, molecular electrostatic potential (MEP) and thermodynamic properties energies were performed by time independent DFT approach. The ^{1}H and ^{13}C NMR chemical shifts of the Phenylhydrazinewere computed and associated with experimental chemical shift.

Keywords: FTIR and FT-Raman B3LYP, GIAO, Phenylhydrazine, HOMO-LUMO.

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Graphical Abstract
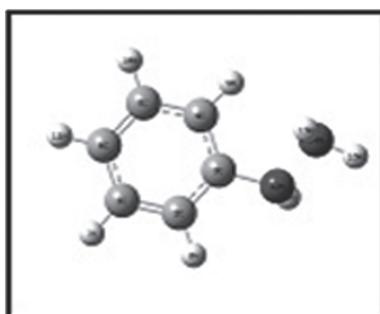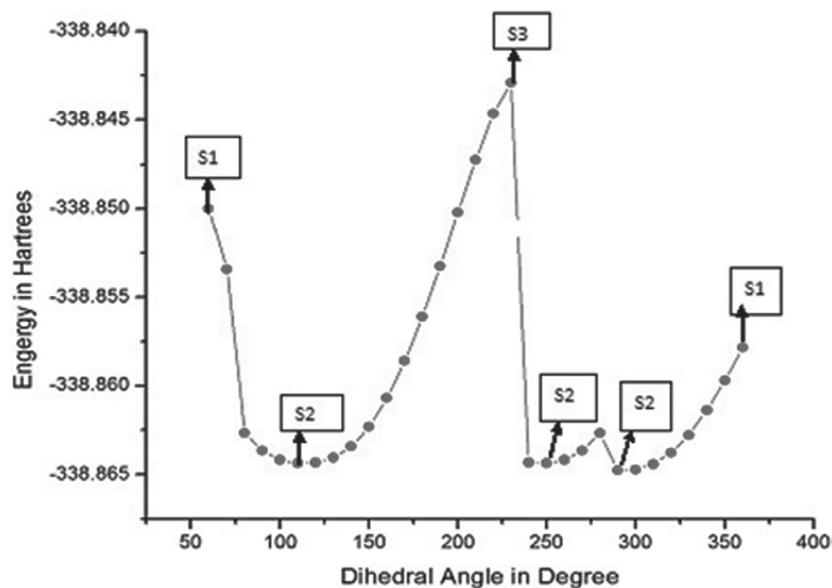
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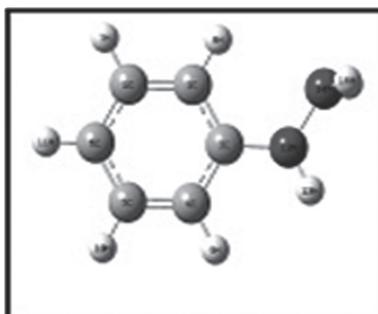
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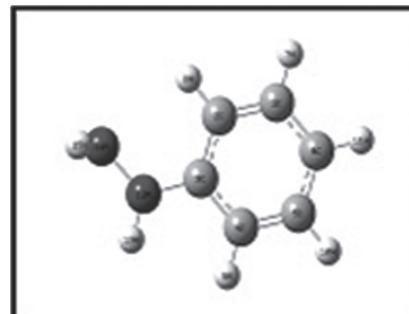
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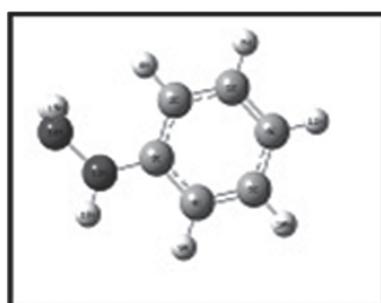
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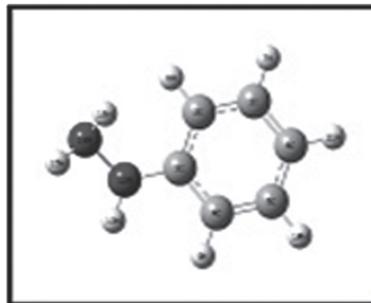
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INTRODUCTION

Phenylhydrazine here after referred as PH, was the principal hydrazine derivative synthesized, specified by Emil Fischer [1]. He used sulfite salts to synthesize phenyldiazonium salt by reduction method. Fischer characterizes sugars through formation of hydrazones with the sugar aldehyde using PH. It is the preliminary material to produce heterocyclicindoles. Indoles are intermediate compound in the synthesis of several types of dyes and medicines. PH is used to form natural mixtures of phenyl hydrazones of simple sugars

[2]. Acute hemolytic anemia is also induced by the use of PH. In jet fuel hydrazine is used as a element because it yields a huge quantity of heat. Compare to hydrocarbon fuels it is less flammable and less volatile. In order to prevent corrosion damage in water boiler feed hydrazine is used as an oxygen scavenger. The retrieval of precious metals hydrazine is used as a reducing agent. In a chain extender in urethane coatings hydrazine used as a polymerization catalyst[3].

Hydrozones are used to treat diseases such as mental disorders, leprosy and tuberculosis. The derivatives of several hydrazones are reported to act as inhibitors of as enzymes [4]. Substituted hydrazides are involved in the therapy of psychotic and neurotic conditions. Carboxylic acids hydrazides are recognized to shows strong antibacterial activities. Durig et al.[5]studied the vibrational spectra of hydrazone. Krishnakumar et al., studied the FTIR and FT-Raman spectra of 2, 4-dinitrophenylhydrazine,and normal coordinate computation by means of standard method to support the vibrational study[6].Okabe et al. [7] reported It's molecular and crystal structure. Arjunan et al.,[8] studied the structure, conformation, vibration, energy, stabilities and thermodynamic properties of benozohydrazide. Sundaraganesan et al [9] reported the enhanced geometry; frequency and intensity of vibrational bands of 2,4-dinitrophenylhydrazine.The infrared spectra of N-benoylhydazine and its uranyl complex have been carried out by Baghat [10]. The characteristics of hydrazones are of significance because of bioticactions and their metal removing properties [11].

Quantum computation and the vibrational studies of PH have been not reported to our knowledge. This insufficiency perceived in the literature exhilarated us to do this spectroscopic computation and investigation.

EXPERIMENTAL DETAILS

The FT-IR spectrum of the compound is recorded in Perkin-Elmer 180 Spectrometer in the range of 4000–400 cm^{-1}. The spectral resolution is ± 2 cm^{-1}. The FT-Raman spectrum of the compound was also recorded in the instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating in the region 3500–50 cm^{-1}, at 1.064μm line widths with 200 mw powers. The spectra were recorded with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ± 1 cm^{-1}. The high resolution ^{1}H and ^{13}C NMR spectra are recorded using 300 MHz and 75 MHz NMR spectrometer respectively.

QUANTUM COMPUTATIONAL METHODS

The complete computation were achieved using Hartree Fock (HF) and Density Functional Theory (DFT) method with Becke's three hybrid function (B3)combined with Lee-Yang-Parr correlations functional constitute B3LYP method on a personal computer using GAUSSIAN 09W [12]package set, appealing gradient geometry optimization [13]. Redundant internal co-ordinates are used to get optimized geometry of the title molecule PH. In order to refine the computed frequency values in correlation with the observed values, it is essential to scale the computed frequencies. Hence, the vibrational frequencies are scaled using suitable scale factor [14,15]. After scaling the computed frequencies, the deviance from the experiential values 10 cm^{-1} less with a few exclusions.

RESULTS AND DISCUSSION

Conformation Study

Conformation study was taken out for phenyl hydrazine by potential energy surface scan to catch all conceivable conformers using HF method with 3-21+G (d, p) basis set. The scans were obtained by minimum the potential energy in all geometrical parameters by changing the rotation angles by steps of 36° in the range of 50–360°rotation about the dihedral angle. The potential energy surface scans with the different structure presented in Fig.1. The rotation about the dihedral angle of the C3-N12-N14-H15 atoms produces different

structure for the title molecule, The lowest energy state of the molecule is represented as S2 with energy -338.865 Hartree, whereas the highest energy states corresponds (S1&S3). The structure S3 has highest energy of -338.843 Hartree than S1 structure. Both the structure is unstable. The brokening of bonds takes Place at 60° having the energy of -338.853 Hartree. From these result it is found that the position S2 having lowest energy and its stable structure. This structure is used for further calculations.
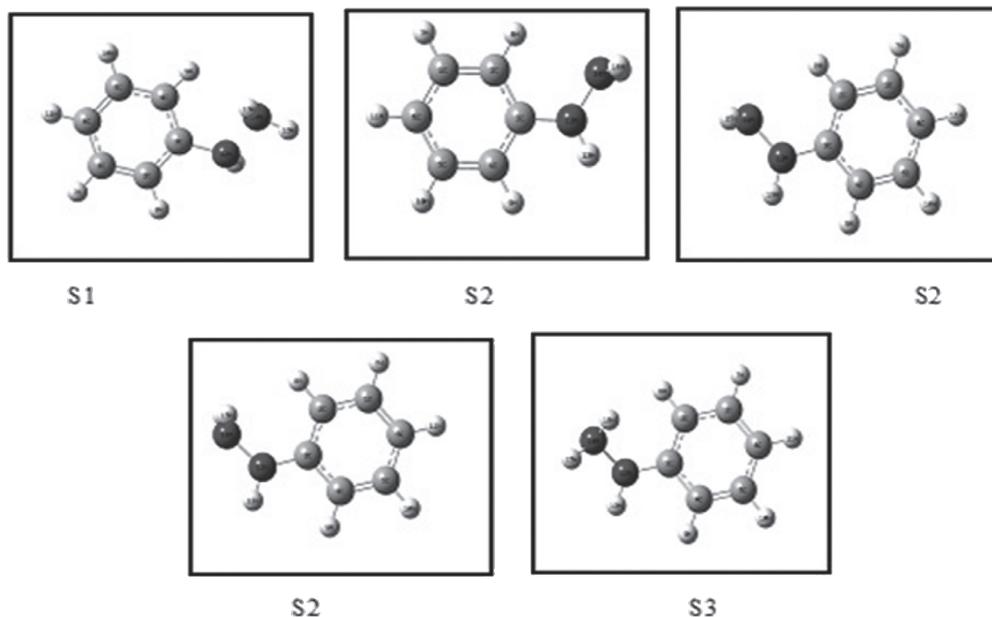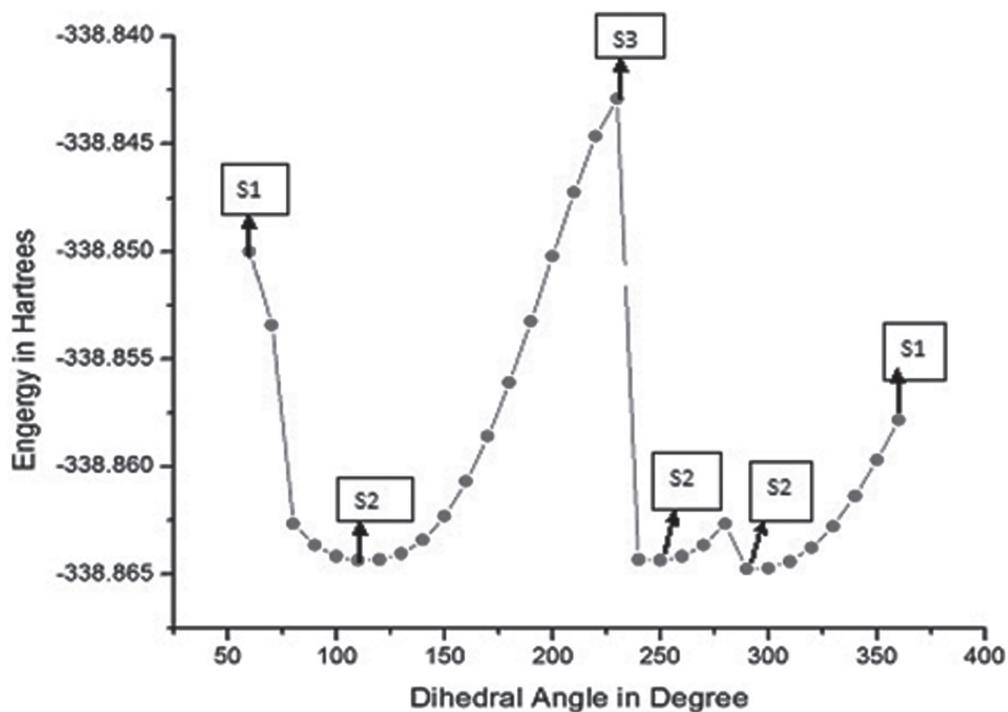
Fig 1:   Comformational Structure Analysis of Phenyl hydrazine

Geometrical Analysis of Molecular Structure

The title molecule Phenylhydrazine (PH) has substituent NH-NH2 at the 3rd position. The enhanced molecular structure along with the atoms numbering is exposed in Fig.2. The enhanced physical parameters of PH computed by HF and B3LYP method with the 6-311G++ (d, p) basis sets are detailed in Table 1. This compares the computed bond distances and angles for PH with X-ray diffraction data available in the literature [16]. The C-C bond distance in HF is 1.37Å and 1.38Å in B3LYP for single bond and 1.39Å in HF and 1.4Å in B3LYP for double bond. C-H bond length is 1.07 and 1.08Å in HF and B3LYP correspondingly. The C-N bond length is 1.39 Å and N-H bond length in HF and B3LYP is 0.9 and 1.0Å respectively. On comparison with the observed data, it is 0.8Å.Comparison of bond lengths in B3LYP with HF, the B3LYP value are superior than the HF and the HF values nearly equal to the experimental outcomes. Inside the benzene ring the CCC bond angles are 120° at C1, C2 C4 whereas at C3 and C6 the bond angle is 118° and 121° at C5. The variations in the bond angle cause the deformation of the structure. This is due to the substitution of NH-NH2 at C3 position.
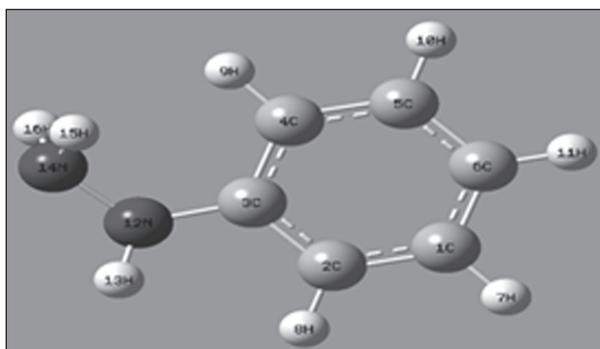
Fig 2:   Enhanced Molecular Structure of Phenyl hydrazine

Table 1: Enhanced Geometrical Parameters for phenyl Hydrazine Calculated at HF/6-311 ++ G (d, p) and B3LYP/6-311 ++ G (d, p) Basis Sets

Geometrical Parameters	Methods		Experimental [a]
	HF/ 6-311++G (d, p)	B3LYP /6-311++ G (d, p)	
Bond length(Å)			
C1-C2	1.378	1.387	1.359
C1-C6	1.389	1.397	1.383
C1-H7	1.075	1.084	0.917
C2-C3	1.397	1.406	1.415
C2-H8	1.076	1.085	0.884
C3-C4	1.389	1.401	1.423
C3-N12	1.396	1.399	1.347
C4-C5	1.388	1.395	1.391
C4-H9	1.073	1.083	1.442
C5-C6	1.380	1.391	1.364
C5-H10	1.076	1.084	0.920
C6-H11	1.075	1.083	-
N12-H13	0.993	1.009	0.872
N12-N14	1.392	1.407	1.405
N14-H15	1.002	1.019	0.908
N14-H16	0.998	1.014	0.887
Bond angle(°)			
C2-C1-C6	120.79	120.71	120.3
C2-C1-H7	119.24	119.27	-
C6-C1-H7	119.95	120.02	119.8
C1-C2-C3	120.54	120.54	121.6
C1-C2-H8	119.96	120.06	122.5
C3-C2-H8	119.49	119.39	-
C2-C3-C4	118.72	118.68	116.4
C2-C3-N12	118.78	119.05	120.3
C4-C3-N12	122.46	122.21	123.3
C3-C4-C5	120.12	120.16	121.1
C3-C4-H9	120.54	120.24	-
C5-C4-H9	119.33	119.59	-
C4-C5-C6	121.13	121.02	121.0
C4-C5-H10	118.93	119.02	121.7
C6-C5-H10	119.92	119.95	-
C1-C6-C5	118.68	118.87	-
C1-C6-H11	120.60	120.51	-
C5-C6-H11	120.71	120.61	-
C3-N12-H13	113.76	114.76	115.2
C3-N12-N14	120.84	121.86	119.8/
H13-N12—N14	110.49	111.05	-
N12-N14-H15	112.03	111.45	112.2
N12-N14-H16	109.99	109.66	103.9
H15-N14-H16	109.49	108.84	100.8

[a]the X-ray diffraction ref [5]

VIBRATIONAL ALLOCATIONS

The point group symmetry of studied compound PH pertains to C1 symmetry. It has 16 atoms, for nonlinear atoms 3N-6 degrees of freedoms are possible. Hence the title molecule has 42 possible modes of vibrations. The 42-standard mode of vibrations are dispersed as

$$\Gamma vib = 29A'+13A''$$

The observed and computed wave numbers using HF and B3LYP methods with 6-311++G (d, p) basis set along with vibrational assignments are presented in Table 2. The observed and computed spectrum for the title molecule is represented in Fig. 3 and Fig. 4

Fig 4:   Experimental[A], Calculated[B] & [C] FTRaman Spectra of Phenyl hydrazine

Fig 3:   Experimental[A], Calculated[B] & [C] FT-IR Spectra of Phenylhydrazine

Table 2:   Systematic Allocation of Theoretical Wave Numbers of Phenyl hydrazine

Modes	species	Experimental		HF 6-311++G(d,p)		B3lyp/6-311++G (d,p)		Vibrational assignment
		IR	Raman	unscaled	scaled	unscaled	Scaled	
	A'	3335 s	3330 w	3842	3484	3594	3443	$NH_2 \nu_{assy}$
	A'	-	3250 w	3808	3453	3545	3396	$NH_2 \nu_{sy}$
	A'		3200 w	3701	3356	3436	3292	$NH \nu$
	A'	3090 s	-	3356	3043	3193	3059	$C\text{-}H \nu$
	A'	-	3060 vs	3348	3036	3186	3052	$C\text{-}H \nu$
	A'	3050 s		3332	3021	3173	3040	$C\text{-}H \nu$
	A'	3020 s		3321	3011	3163	3030	$C\text{-}H \nu$
	A'		2980 vw	3311	3002	3152	3020	$C\text{-}H \nu$
	A'	1600 vs		1838	1667	1695	1624	$C{=}C \nu$

Modes	species	Experimental		HF 6-311++G(d,p)		B3lyp/6-311++G (d,p)		Vibrational assignment
		IR	Raman	unscaled	scaled	unscaled	Scaled	
	A'		1590w	1787	1620	1643	1574	C=C ν
	A'	1495 s	1495 w	1772	1607	1626	1558	C=C ν
	A'	1450 w	-	1669	1513	1528	1464	C-C ν
	A'		1430 vw	1647	1493	1524	1460	C-C ν
	A'	1390 w	1390 vw	1581	1433	1461	1400	C-C ν
	A'	1305s		1460	1324	1359	1302	C-N ν
	A'		1300 w	1434	1300	1335	1279	N-N ν
	A'	1270 s	1270 w	1403	1272	1319	1264	N-H β
	A'	1180 s	-	1333	1209	1294	1240	N-H β
	A'	-	1170 w	1289	1169	1201	1151	N-H β
	A'	1160 w	1160 w	1261	1143	1180	1130	C-H β
	A'	-	1150 s	1194	1083	1165	1116	C-H β
	A'	1130 w	-	1176	1066	1099	1053	C-H β
	A'	1110 w	-	1116	1012	1047	1003	C-H β
	A'	1080 w	1080 w	1103	1000	1005	963	C-H β
	A'	1010 w	1010 w	1089	987	985	944	C-N β
	A'	-	990 vs	1070	970	967	926	N-N β
	A''	930 s	-	1014	919	906	868	N-H γ
	A''	890 s	-	985	893	881	844	N-H γ
	A''	815 w		921	835	828	793	N-H γ
	A''	-	805 vs	887	804	817	783	C-H γ
	A''	750 vs	750 vw	841	763	762	730	C-H γ
	A''	690 vs	690 vw	767	695	704	674	C-H γ
	A''	-	650 w	714	647	648	621	C-H γ
	A''	-	610 s	674	611	632	605	C-H γ
	A''		580 w	595	539	537	514	C-N γ
	A''	570 s	-	562	510	520	498	N-N γ
	A'	500 s	500 w	477	432	446	427	CCC β
	A'	430 w		455	413	420	402	CCC β
	A'	-	280 w	396	359	346	331	CCC β
	A''	-	220 w	275	249	252	241	CCC γ
	A''	-	190 s	218	198	200	192	CCC γ
	A''	-	-	101	92	107	103	CCC γ

ν- stretchingν$_{assy-}$-asymmetric stretching,, β-in-plane bending, γ-out of plane bending

C-H Vibrations

The stretching vibrations carbon-hydrogen are perceived in the region 3000–3100 cm^{-1} for all the aromatic compounds [17]. In the current investigation hydrogen atom attached about the ring and lead to 5 modes of C-H stretching, 5 in-plane and 5 out-of-plane bending vibrations. C-H stretching vibrational band for the PH are perceived at 3090,3060,3050,3020 and 2980 cm^{-1}.

Except one band remaining bands are in probable region. The decrease in wave number is because of the NH-NH2 group substitution of in benzene ring. The scaled computed values are 3059, 3052, 3040, 3030 and 3020 cm-1in B3LYP6-311++G (d, p). For all aromatic compound the Carbon–Hydrogen in-plane and out-of-plane bending vibrations are generally originate in the range from 1300cm^{-1}to 1000 cm^{-1} and 1000-750cm^{-1}, respectively [18,19].

In case of PH the following frequency1160, 1150, 1130, 1110 and 1080 cm^{-1} for in-plane bending and 805, 750, 690, 650, and 610   cm^{-1} are allocated to C-H out-of-plane bending in B3LYP6-311++G (d, p). The in-plane bending vibration of C-H is in the predictable region. Whereas in the out of plane bending the last four band having lower frequency this may due to the NH-NH2 group substitution.

C -C, C=C Vibrations

Normally in aromatic compounds the CC stretching vibrations are originate in the region of 1430–1650 cm^{-1}. Conferring to Socrates [20], the occurrence CC initiates an intense doublet creation about the region1625–1575 cm^{-1}. The six ring carbon atoms experience combined vibrations which are usually called as ring vibrations provide all-out of four vibrations in the region 1660–1420 cm^{-1}. As per literature [21, 22], the prominent peaks at 1600 1590 and 1495 cm^{-1} to C=C and 1450, 1430 and 1390cm^{-1} are allocated to C-C single bond stretching. The calculated scaled wave numbers are at 1624, 1574 and 1558 cm^{-1} in B3LYP6-311++G (d, p) are due to an intense C=C stretching and1464, 1460 and 1400 cm^{-1} in B3LYP6-311++G (d, p) are owing to an intense C−C benzene ring vibrations for PH. All the bands are in expected region.

Hydrazine Group (-NH-NH2) Vibration

The hetro aromatic compound comprising an N-H group instigates its elongating absorption in the range 3500- 3200 cm^{-1}. This is common region of presence for NH2. [22] The frequency experiential at 3335 cm^{-1} in the IR spectrum is allocated to the NH2 asymmetric stretch of **PH**. The symmetric stretching vibration of NH2 is experiential at 3250 cm^{-1}. The N-H stretching perceived at 3200cm^{-1} in FT-Raman. Arjunan et al [08] allocated the NN stretch at 1165 cm^{-1} for benzohydrazide. In the current case the N-N stretch allocated at 1300 cm^{-1} in FT-Raman.

Among the other amino group, the very intense band in IR at 1270 and 1180cm^{-1} is assigned to the –NH2 in plane bending vibration. The NH in-

plane bending vibration assigned at 1170cm^{-1} in FT-Raman. The out of plane bending of NH are assigned at 930, 890, and 815 cm^{-1}.The further essential bands of amino group are experiential in the expected region and are existing in Table 2.

C N Vibrations

The conformation of C-N vibrations is a tough job, subsequently combining of numerous bands are conceivable in this area. Silverstein et al. [24] allocated C-N elongating absorption for aromatic amines in the range 1380–1270 cm^{-1}. The band experiential at 1368cm^{-1} is allocated to CN elongation for benzamide[25]., Similarly the CN elongating vibration is originated at 1382 and 1307 cm^{-1} for benzotrizole. In the current study, a intense vibration at 1305 cm^{-1} in FT-IR spectrum has been allocated to CN elongating vibrations. The theoretically computed value of C-N stretching vibration at 1302 cm^{-1} precisely matches with experimental observed value. The in-plane and out-plane bending vibrations are 1010 and 580 cm^{-1}.

MULLIKEN ATOMIC CHARGES

Significant effects on the vibrational spectra are influenced by charge spreading on the molecule. The Mulliken charge distributions of PH are computed using B3LYP method with 6-311G++ (d, p) basis sets are tabulated in Table 3. The graphic of atomic charges plot is shown in Fig. 5. The outcomes demonstrate that substitution hydrazine on the aromatic ring leads to a redeployment of electron density. From Table 3 more positive charges are observed for all the hydrogen atoms, similarly more negative charges distributed around carbon and nitrogen atom. The more negative values on N14 atom of NH-NH2 group leads to a rearrangement of electron density. Alternatively atomic charges of hydrogen (H13, H15 and H16) in the NH-NH2 group are also almost equal but H15 has peripheral change with H13 and H16.
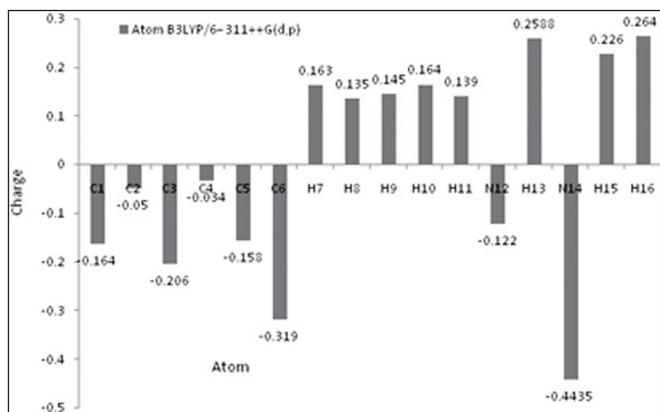
Fig 5:   Mulliken Atomic Charge Calculated using B3LYP/6-311++G (d, ρ) for Phenylhydrazine

Atom	Charges
	B3LYP/6−311++G(d,p)
C1	-0.164
C2	-0.050
C3	-0.206
C4	-0.034
C5	-0.158
C6	-0.319
H7	0.163
H8	0.135
H9	0.145
H10	0.164
H11	0.139
N12	-0.122
H13	0.258
N14	-0.443
H15	0.226
H16	0.264

Table 3: Mulliken Atomic Charges of Phenyl hydrazine using B3LYP/6−311++G(d,p) Basis

HOMO–LUMO AND UV-VIS INVESTIGATION

The electronic structure of **PH** are calculated at TD-SCF method using B3LYP/6-311++G (d, p) basis set. The computations are made with gas and solvent (DMSO and chloroform) phase. The computed excitation energies, oscillator strength (f) and wavelength (λ) and major contributions

are presented in Table 4. The intense transitions at 268.21 and 265.65 nm with an f = 0.0557and 0.0522 in gas and DMSO phase respectively, allocated to π-π* transition. It is observed that the computation made at DMSO and gas is closer than chloroform phase. The relation of excitation energy with epsilon is presented in Fig 6. The HOMO signifies the capability to contribute an electron, LUMO is accepting electron. The three-dimensional designs of the molecular orbitals for PH molecule exposed in Fig.7. From the Fig.7, HOMO is mostly confined over the whole molecule and LUMO is confined on ring except NH-NH2 group. The HOMO and LUMO energy gap are -5.94 eV and -0.52 eV in gas phase (Table 5). The DFT level computed energy gaps 5.42 eV shows the dropping of energy gap.
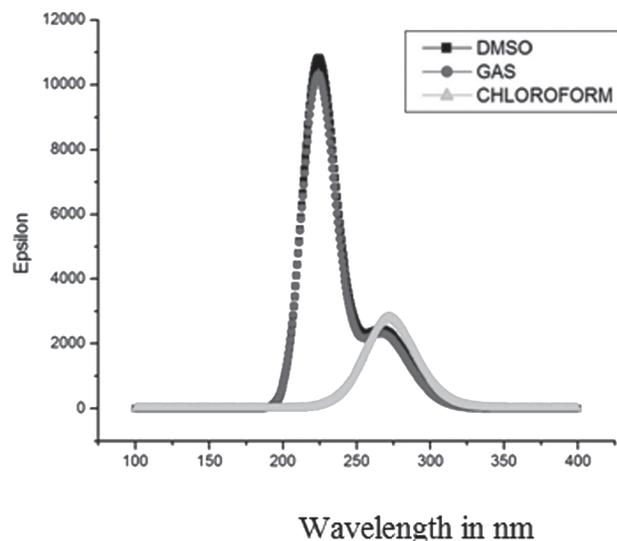
Fig 6: UV –Vis Spectrum Calculated using B3LYP/6-311++G(d, ρ) for Phenylhydrazine

Table 4:   UV-Visible Spectral Value of Phenyl hydrazine

Time Dependent-Density Functional Theory at B3LYP/6-311 ++G(d,p)									
Gas			DMSO			Chloroform			Gas
Wave lengths λ (nm)	Excitation Energy (eV)	Oscillator Strengths (f)	Wave lengths λ (nm)	Excitation Energy (eV)	Oscillator Strengths (f)	Wave lengths λ (nm)	Excitation Energy (eV)	Oscillator Strengths (f)	Major contribution a
268.21	4.62	0.0557	268.43	4.61	0.0585	272.71	4.54	0.0664	H → L (91%)
223.88	5.53	0.2533	224.30	5.52	0.2659	266.92	4.64	0.0016	H → L+1→ (86%)
209.99	5.90	0.0029	210.22	5.89	0.0031	244.12	5.07	0.0071	H → L+2→(66%) H → L+3(20%)

ªH → HOMO; L → LUMO

Table 5:   Computed Energies at Different Solvent Phase for Phenyl hydrazine

TD-DFT/B3LYP/ 6-311 ++G(d,p)	Gas	DMSO	Chloroform
E_{HOMO}	-5.94	-5.91	-5.90
E_{LUMO}	-0.52	-0.51	-0.48
$E_{HOMO-LUMO\ gap}$ (eV)	5.42	5.40	5.41
E_{HOMO-1} (eV)	-7.17	-7.17	-7.13
E_{LUMO+1} (eV)	-0.24	-0.24	-0.25
$E_{HOMO-1-LUMO+1\ gap}$ (eV)	6.93	6.93	6.88
Chemical hardness η (eV)	2.71	2.70	2.705
Electro negativity χ (eV)	-3.22	-3.21	-3.19
Chemical Softnessξ(eV)	0.184	0.185	0.185
Electrophilicityindexω (eV)	1.912	1.908	1.880
Dipole moment (Debye)	0.9319	0.9264	0.8337

NATURAL BOND ORBITAL ANALYSIS

By means of second-order perturbation theory intra and inter molecular interaction, the stabilization energy of title molecule was performed. The stabilization energy E(2) linked with electron donor and acceptor is calculated using the below relation as [26, 27]

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i}$$

The outcomes of second-order perturbation theory examination of the Fock Matrix at B3LYP/6-31G++ (d,p) method and basis set are presented in Table 6.

The electron contribution and acceptance are intensive when the $E^{(2)}$ value is large. The intermolecular interactions of π-π* transition from C1-C2 → C3-C4 (21.64KJmol⁻¹), C5-C6 (16.32KJmol⁻¹); C3 − C4 → C1-C2 (16.31 KJmol⁻¹) C5- C6 (23.49 KJmol⁻¹); C3-C4 → C1-C2 (18.25 KJmol⁻¹), C5-N6 (26.53 KJmol⁻¹)

and C11-O12 (20.35 KJmol^{-1}) and π bonds in benzene ring indicates strong delocalization. σ-σ* transition taken from various bonds in title molecule σ (C1-C2) with antibonding σ* (C1-C6), (C1-H7), (C2-C3), (C3- N12) and (C2-H8) contribution of energies 2.77, 0.86, 3.13 and 1.24 KJmol^{-1} correspondingly. The electron donating from the LP N12 to the antibonding π*

(C3-C4) leads to moderate stabilization energy of 29.83 KJmol^{-1} is shown in Table 6. On comparing with UV-V is absorption spectrum only two transitions are prominent the transition from C1-C2 to C3-C4 and C3-C4 to C5-N6 having high stabilization energy.

Table 6: **NBO Analysis Computed by B3LYP6-311++G (d, p) Basis Sets for Phenyl hydrazine**

Donor (i)	Type	ED/e	Acceptor (J)	Type	ED/e	E(2) (KJmol-1)
C1-C2	σ	1.97797	C1-C6	σ*	0.01629	2.77
			C1-H7		0.01330	0.86
			C2-C3		0.02251	3.13
			C2-H8		0.01394	1.24
			C3-N12		0.03559	3.49
			C6-H11		0.01352	2.29
C1-C2	π	1.71706	C3-C4	π*	0.33064	21.64
			C5-C6		0.34582	16.32
C1-C6	σ	1.9789	C1-C2	σ*	0.01386	2.81
			C1-H7		0.01330	0.91
C2-C3	σ	1.97044	C1-C2	σ*	0.02251	2.88
			C3-C4		0.02430	4.00
			N12-N14		0.0109	3.28
C3-C4	σ	1.9722	C2-C3	σ*	0.02251	4.00
C3-C4	π	1.65089	C1-C2	π*	0.33064	16.31
			C5-C6		0.34582	23.49
C4-C5	σ	1.97757	C3-C4	σ*	0.02430	3.23
			C3-N12		0.03559	3.94
C4-H9			C2-C3		0.02251	4.27
			C5-C6		0.01613	3.67
LP(N12)			C3-C4		0.02430	29.83

LUMO+1= (-0.24eV)

LUMO = (-0.52eV)

ΔE=5.42eV

ΔE = 6.93eV

HOMO = (-5.94eV)

HOMO -1= (-7.17eV)
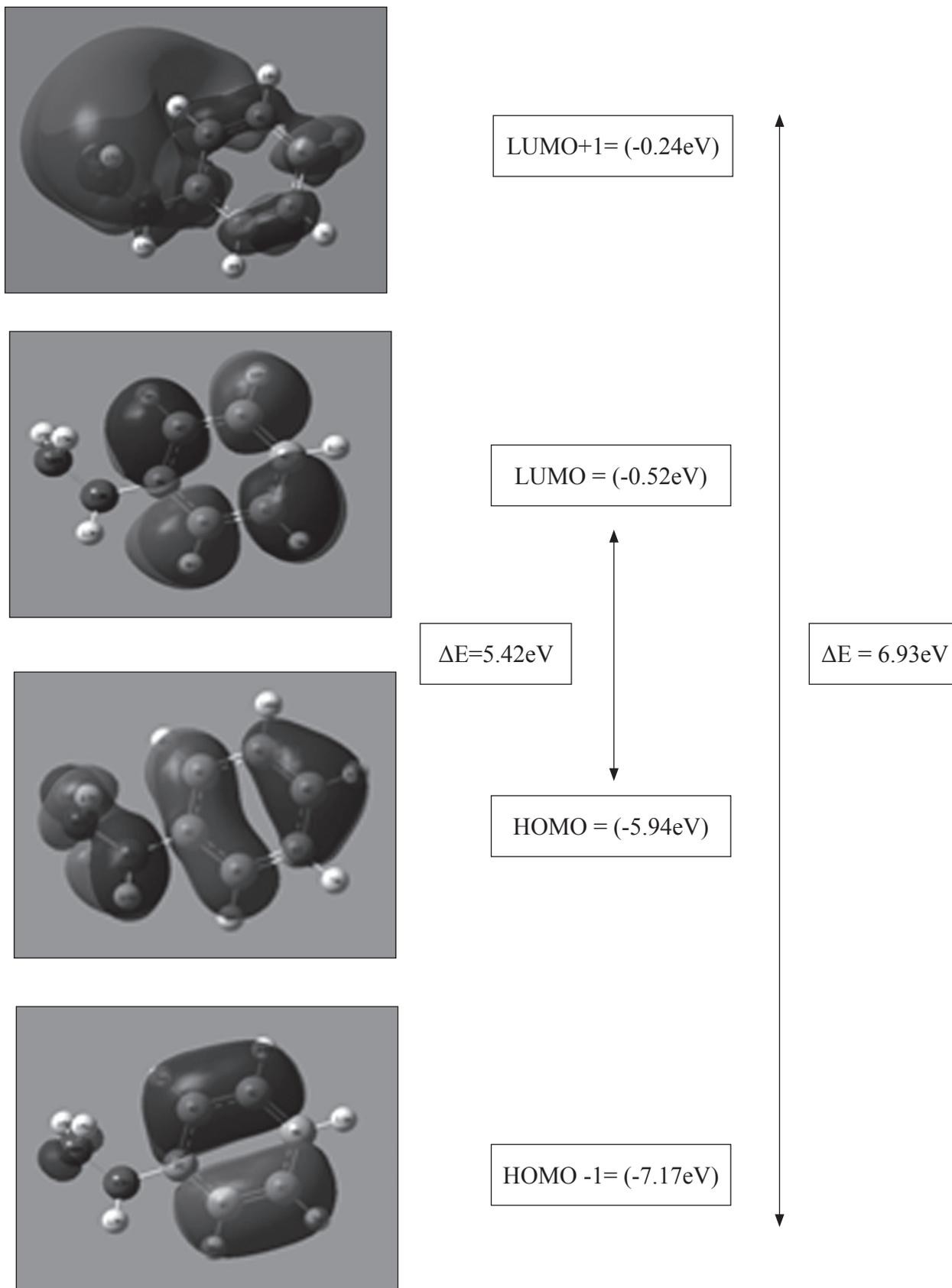
Fig 7:   Frontier Molecular Orbitals of Phenyl hydrazine

MEP EXAMINATION

To forecast responsive locations for electrophilic and nucleophilic occurrence of PH, MEP was computed at the B3LYP/6-31G++(d) and shown in Fig 8. The negative (red) regions of MEP were connected to electrophilic site and the positive (blue) regions to nucleophilicsite [28, 29]. The negative regions are mostly concentrated on nitrogen and carbon atoms. A supreme positive region is concentrated on the hydrogen atoms in NH2cluster of the PH representing a conceivable location for nucleophilic attack. The non-covalent interactions of the compound are indicated by electrophilic and nucleophilic sites. The contour map and electron density are also shown in Fig 8.

(c)

(d)

(a)

(b)
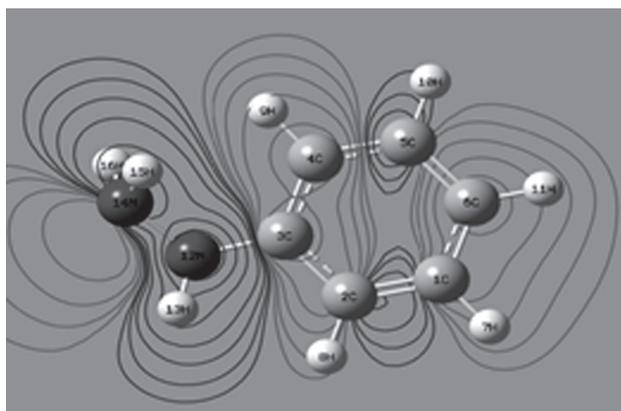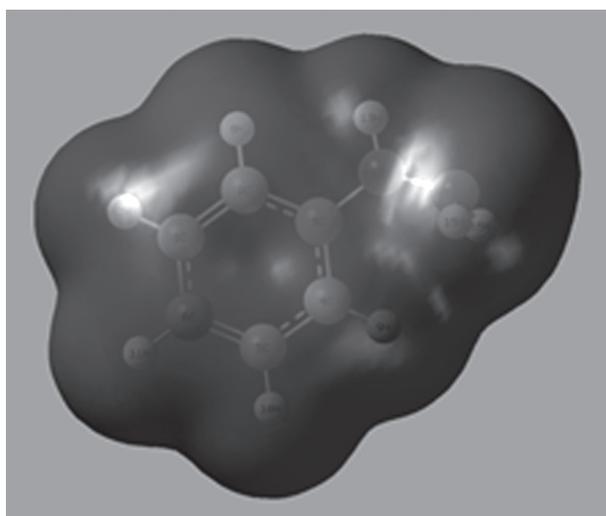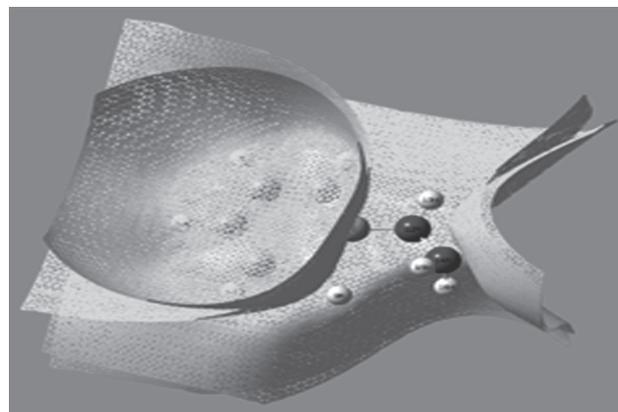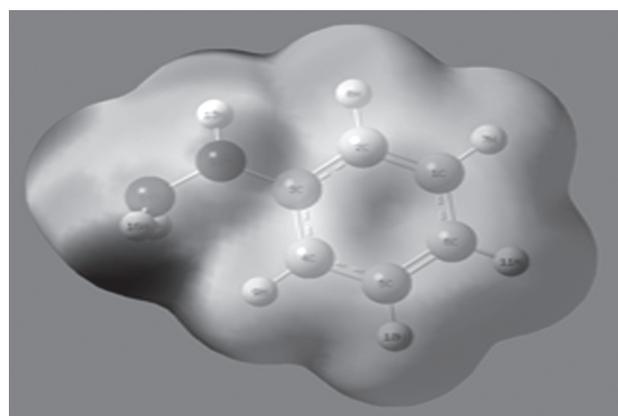
Fig 8: (a) Contour map, (b) Electron density (ED), (c) Electrostatic Potential Map (ESP) and (d) Molecular Elecrosatic Potential Map (MEP) for Phenylhydrazine Caculated at b3lyp6-311++G(d,p)

NMR INVESTIGATION

The structure conformations of molecule are elucidated using NMR spectroscopy. To provide an clear allotment and examination of ^{13}C and ^{1}H NMR spectra, theoretical computation on chemical shift of the PH are done using gauge independent atomic orbitals with B3LYP/6-311++g(d,p) basis set[30]. The calculation were done consider into account IEFPCM/DMSO/Chloroform solvent effect. The theoretical ^{1}H and ^{13}C NMR chemical shifts have given in Table 7 and the experimental spectra are given in Fig.10 & 11 respectively.

Ring carbons give indications in overlay region of the spectrum with chemical shift values from 100 to 150 ppm. In the current study, the observed chemical shift values of ring carbons are found in the region 112 to 151 ppm. The aromatic hydrogen atoms have the chemical shift around 7.15-6.66 ppm. Comparative chart of experimental and calculated chemical shift are presented in Fig. 12. It reveals that chemical shift determined in different solvent through gauge independent atomic orbitals (GIAOs) using B3LYP63-11++G(d,p) basis set are in good covenant with observed value.

In the present molecule the carbon atom at C3 position observed to be large chemical shift than the surrounding carbon atoms. The attachment of electronegative atom at C3 position causes more shifts at C3. The carbon atoms C2, C4, and C6 have moderate shift of 114, 109 and 119 ppm respectively. The hydrogen atoms present around the benzene ring have more shift than the hydrogen surrounded by electronegative nitrogen atoms. In the present investigation H13, H15 and H16 having very small shift of 2 to 4 ppm.
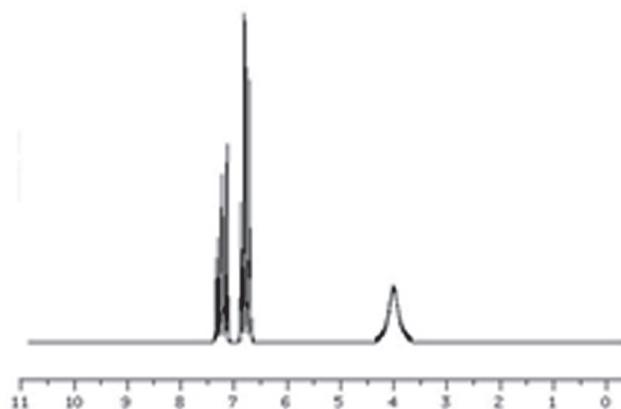
Fig 10:   Experimental H1 NMR Spectrum of PH
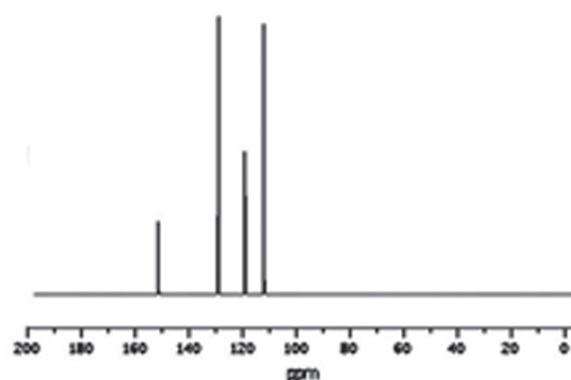
Fig 11:   Experimental C13 NMR Spectrum of PH
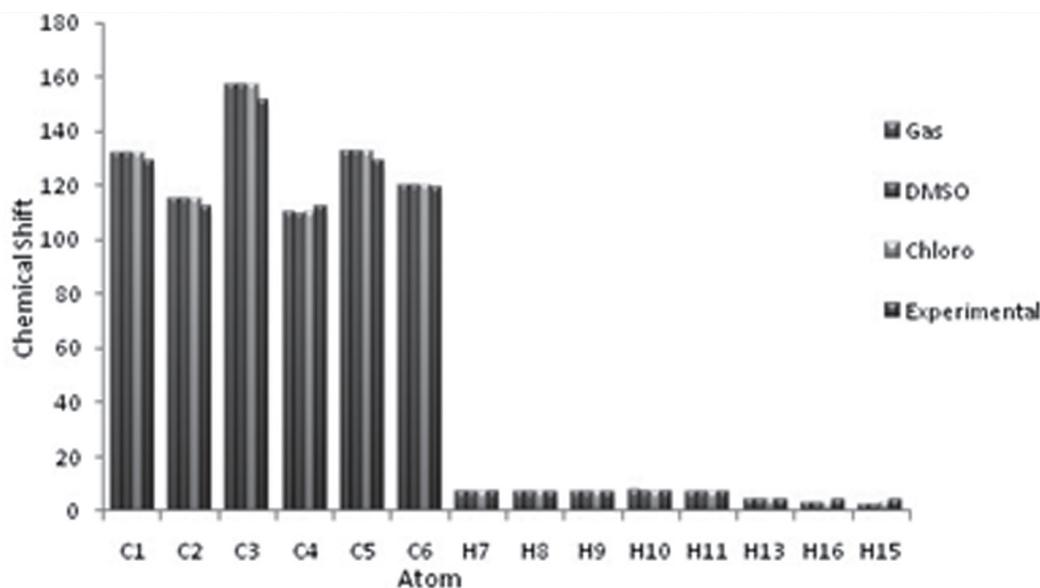
Fig 12:   Comparative Chart of Observed and Computed NMR Chemical Shift for PH

Table 7: ^{13}C & ^{1}H Chemical Shift δ(ppm) of Phenyl hydrazine by TMS B3LYP/6-311G++ (2d,p) Method

Atom Position	Chemical shift δ(ppm)			Experimental
	Gas	CDCl3	DMSO	
C1	131.49	131.58	131.52	129.08
C2	114.84	114.68	114.79	112.06
C3	156.85	156.77	156.89	151.35
C4	109.8	109.52	109.89	112.06
C5	132.30	132.26	132.29	129.08
C6	119.81	120.07	119.90	119.12
H7	7.15	7.08	7.12	7.21
H8	6.66	6.62	6.67	6.76
H9	6.73	6.62	6.74	6.76
H10	7.32	7.27	7.13	7.21
H11	6.73	6.72	6.74	6.80
H13	4.37	4.28	4.37	4.0
H16	3.03	2.93	2.17	4.0
H15	2.19	2.07	3.00	4.0

THERMODYNAMIC PROPERTIES

Using B3LYP/6-311G++(d,p) method and basis set the thermodynamical variables heat capacities (C^0p,m), entropies (S^0m) and enthalpy changes (ΔH^0m) for PH were obtained and listed in Table 8. It is observed that the computed thermodynamic function is increased with rise in temperature in the range 50 to 250K. This increase in value due to molecular vibration increases with rise in temperature [31]. The equation associated with these thermodynamical variables are well-fitting by quadratic equation and the consistent fitting factor are 0.9979, 0.9988 and 0.9986 for heat capacities, entropies, enthalpy changes respectively. The consistent fitting equations are given below and the corresponding graph shows in Fig. 9

C^0p,m = 4.36033 + 0.04898T + 9.451933.615 × 10−5T2
(R2 = 0.9979) (SD = 0.14228)

S^0m = 47.5944 + 0.14144T − 9.10509 × 10−5T2
(R2 = 0.9988) (SD = 0.4429)

ΔH^0m = 84.325 + 0.00149T + 4.22395 × 10−5T2
(R2 = 0.9986) (SD = 0.02324)

Obtained thermodynamic data give useful statistics aimed at the advance investigation on the PH. According to the second law of thermodynamics in thermo-chemical field these data can be used to compute the other thermodynamic energies[32].

Table 8: Heat Capacities (C^0p,m), Entropies (S^0m) and Enthalpy Changes (ΔH^0m) using B3LYP/6-311 ++G (d,p) Level for Phenyl hydrazine
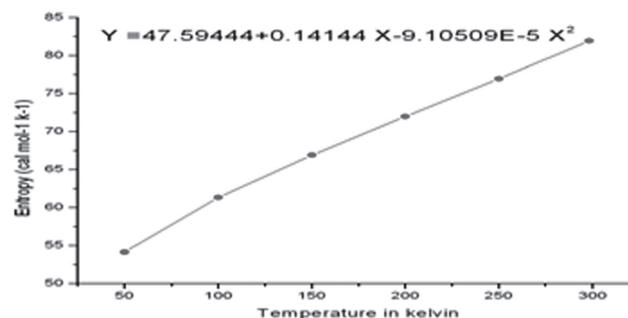
T (k)	Heat Capacities (cal mol-1 k-1)	Entropies (cal mol-1 k-1)	Enthalpy Changes (kcal mol-1)
50	7.132	54.13	84.49
100	10.09	61.32	84.920
150	13.75	66.89	85.51
200	18.01	71.99	86.30
250	22.65	76.94	87.32
298.15	27.27	81.93	88.54
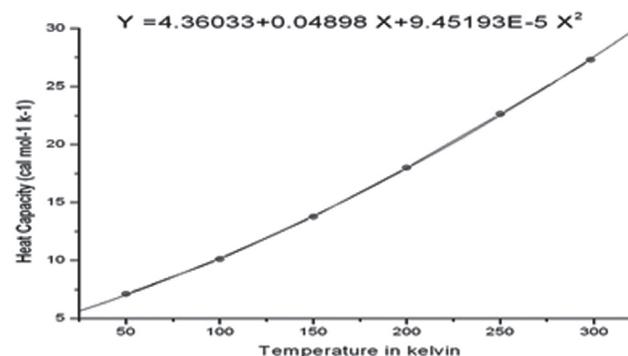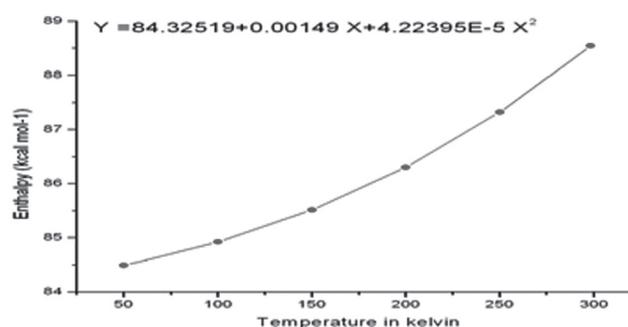
Fig 9: Association Diagram for Entropy, Enthalpy and Heat Capacity

CONCLUSION

Using Hartree-Fock and Density functional theory adopting B3LYP 6-311G++ (d, p) method and basis sets, the IR and Raman spectrum are analyzed and through assignment of vibrations are done. The variation of the wave number between observed and computed is found to be small for most of fundamental modes in B3LYP 6-311G++ (d, p) method. Therefore, the outcomes presented in this effort for PH specify that B3LYP 6-311G++ (d, p) level of theory is consistent. Thermodynamical variables heat capacities (C^0p,m), entropies (S0m) and enthalpy changes (ΔH^0m) for PH were obtained. The consistent fitting factor are 0.9979, 0.9988 and 0.9986 for heat capacities, entropies, enthalpy changes respectively. From NBO, UV-Vis and HOMO-LUMO analysis, it is concluded that transfer of charge exists within the molecule corresponds to π-π* transition. Molecular electrostatic potential graph shows possible site for chemical reaction.

ACKNOWLEDGEMENTS

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